(reduction of methyl 4-benzoylbenzoate by $NaBH_4$). Among other secondary photoproducts found in small amounts was a mixture of pinacols. These were confirmed by synthesis of a similar pinacol mixture upon irradiation of methyl 4-benzoylbenzoate in isopropyl alcohol.

**Photolysis of *tert*-Butyl 4-(2′,4′,6′-Trimethylbenzoyl)perbenzoate (Ib) in $CH_3OD$.** After photolysis of the perester (300 mg in 20 mL of $CH_3OD$) for 1 h, the following products were found: 14.1% of $CO_2$, 15.6% of phenyl mesityl ketone, 56.6% of starting perester, and 21.8% of the corresponding acid.

The phenyl mesityl ketone showed no deuterium incorporation (mass spectrometry). The perester showed no deuterium incorporation (NMR).

The recovered perester was irradiated again in cyclohexane solution (25 mL) for 4 h. The following products were found: carbon dioxide, 44%; bicyclohexyl (21 mg); mesityl phenyl ketone (52%); and the corresponding acid, 46%. No deuterium incorporation in the mesityl phenyl ketone was found.

**Photolysis of Perester IV in MeOH.** Perester IV (1.0 mmol) was irradiated for 85 min in 30 mL of MeOH. The following products were obtained: carbon dioxide, 11%; butyrophenone, 10% (confirmed by high-pressure LC); methyl *p*-butyrylbenzoate (25%) (mp 83–85 °C from hexane) (confirmed by independent synthesis); and *p*-butyrylbenzoic acid (52%) (confirmed by preparation of the methyl ester. No products of a Norrish type II reaction could be found.

**Determination of Photodecomposition Rate and Quantum Yields.** A solution of perester (2 mL) in the appropriate solvent was placed in Pyrex tubes (12-mm diameter), degassed, and sealed under vacuum. Three cycles of freeze–thaw removed dissolved oxygen. The tubes were placed in a merry-go-round around a water-cooled light source, removed at different predetermined intervals, and kept frozen in liquid nitrogen in the dark until analysis was done. The estimation of perester was done by quantitative IR, monitoring the carbonyl peak at 1770 $cm^{-1}$. None of the products of decomposition or the solvent interfered at this wavelength. Absorbance was measured with a 0.1-mm NaCl cell against solvent reference. With every run, two tubes containing actinometric solutions (benzophenone (0.1 M) and benzhydrol (0.05 M) in benzene) were also irradiated. The light intensity and quantum yield of benzophenone loss were measured by measuring the decrease in benzophenone content spectrophotometrically (using the benzophenone peak at 345 nm).

**Polymerization Studies.** Commercial methyl methacrylate monomer was washed three times with 2% NaOH solution to remove stabilizer. It was then washed with distilled water three times, dried with molecular sieves, and distilled under vacuum before use. Polymerization solutions were prepared in cylindrical tubes which were degassed and sealed. The amount of polymer formed was determined by precipitating the polymer with an excess of methanol, washing with methanol, and filtering through fine sintered crucibles (previously weighed) followed by drying in a vacuum oven. The irradiation condition was the same as that in the decomposition rate studies.

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**Registry No.** Ia, 71616-77-8; Ib, 71616-78-9; Ic, 71616-79-0; Id, 71616-80-3; II, 24546-34-7; III, 25251-51-8; IV, 71616-81-4; *p*-benzoylbenzoic acid, 611-95-0; benzophenone, 119-61-9; 4-(2′,4′,6′-trimethylbenzoyl)benzoic acid, 65414-32-6; mesityl phenyl ketone, 954-16-5; *p*-butyrylbenzoic acid, 71616-82-5; methyl *p*-butyrylbenzoate, 71616-83-6; butyrophenone, 495-40-9; $Bz_2O_2$, 94-36-0; 4-(4′-methoxybenzoyl)methylbenzoate, 71616-84-7; *tert*-butyl hydroperoxide, 75-91-2; *o*-benzoylbenzoic acid, 85-52-9; bicyclohexyl, 92-51-3.

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[21] Toxicological data on compounds herein were obtained from: N. I. "Dangerous Properties of Industrial Materials", 3rd ed.; Van Nostrand-Reinhold: Princeton, N. J., 1968.

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# Stereochemistry of Ring Enlargement by [2,3] Sigmatropic Rearrangement of Cyclic Sulfonium Ylides. Synthesis of 5-Methylthiacycloalk-4-enes

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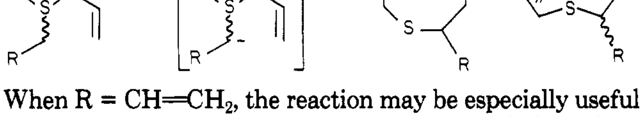
Sulfonium ylides generated in situ from *r*-1,*t*-2-dimethyl-2-vinylthiolanium (**1b**), *r*-1,*t*-2-dimethyl-2-vinylthianium (**2b**), and *r*-1,*c*-2-dimethyl-2-vinylthianium (**2c**) hexafluorophosphates undergo highly stereoselective but nonstereospecific [2,3] sigmatropic ring enlargement. The six-membered methylide from **2b**, where the carbanionic and vinyl moieties are on the same side of the ring, reacts faster than the ylide from **2c**; however, both give (*E*)-5-methylthiacyclonon-4-ene as the exclusive product. The five-membered methylide from **1b** ring expands, giving a ca. 17:1 mixture of (*Z*)- and (*E*)-5-methylthiacyclooct-4-ene. The isomeric methylide from **1c**, where the carbanionic and vinyl moieties are on opposite sides of the ring, does not appreciably react in the [2,3] sigmatropic fashion but undergoes *β*-elimination, probably by the *α′*,*β* mechanism. The results are rationalized in terms of ground-state conformational effects, in accord with an early transition state for the [2,3] sigmatropic rearrangement of allylic sulfonium ylides.

The well-known [2,3] sigmatropic rearrangement of allylic sulfonium ylides to homoallylic sulfides[1] has been recently exploited[2] for a three-carbon ring enlargement involving stabilized (R = COPh, COOEt)[3] as well as unstabilized (R = H, $CH_3$, Ph)[4] sulfonium ylides.



When R = CH=CH$_2$, the reaction may be especially useful for a ring-growing sequence since the expanded product has the 2-vinyl moiety already built in and may be further expanded in three carbon unit steps.[5,3b]

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[1] (a) Baldwin, J. E.; Hackler, R. E.; Kelly, D. P. *Chem. Commun.* **1968**, 538. (b) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147, and references therein.

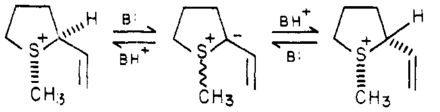
[2] Vedejs, E.; Hagen, J. P. *J. Am. Chem. Soc.* **1975**, *97*, 6878.

[3] (a) Vedejs, E.; Hagen, J. P.; Roach, B. L.; Spear, K. *J. Org. Chem.* **1978**, *43*, 1185. (b) Vedejs, E.; Arco, M. J.; Powell, D. W.; Renga, J. M.; Singer, S. P. *Ibid.* **1978**, *43*, 4884. (c) Vedejs, E.; Arco, M. J.; Renga, J. M. *Tetrahedron Lett.* **1978**, 523.

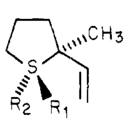
[4] (a) Cerè, V.; Pollicino, S.; Sandri, E.; Fava, A. *J. Am. Chem. Soc.* **1978**, *100*, 1516. (b) Cerè, V.; Paolucci, C.; Pollicino, S.; Sandri, E.; Fava, A. *J. Org. Chem.* **1978**, *43*, 4826.

The stereochemical aspects of this ring enlargement have not been yet elucidated. The reaction appears to be stereoselective, the geometry of the product olefin being largely dictated by the ring size, i.e., predominantly *Z* for the eight-membered olefin, $n = 1$,[2,3a,4b] and predominantly *E* for the larger sizes, $n = 2, 3$.[3b,4b] However, the question of stereospecificity, i.e., the relation between the geometry of the product and that of the starting ylide (or the sulfonium salt precursor), remains unanswered.

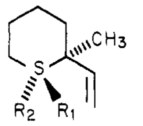
We have previously reported about an (unsuccessful) attempt to establish such a relation, where the same product distribution (85/15 *Z*/*E* thiacyclooct-4-ene) was obtained by starting from pure *trans*-1-methyl-2-vinylthiolanium hexafluorophosphate or from a 50:50 mixture of trans and cis salts.[4b] The reason of such failure was traced to an isomerization of the starting sulfonium salt occurring faster than ring expansion.[4b] Furthermore, it was shown by deuterium labeling experiments that the isomerization was occurring via rapid and reversible abstraction of the allylic proton at $C_2$.[4b]



To answer the question of which ylide yields which geometrical isomer of the ring expanded olefin, one requires a substrate where this isomerization pathway is precluded. The obvious solution is one where the acidic proton at $C_2$ is replaced by a methyl or other similar group. While, in such a substrate, other conceivable isomerization mechanisms would still be allowed (pyramidal inversion of the S atom either in the ylide[6] or in the cation,[7] or ionization of the $C_2$–S bond[8] to reversibly give a tertiary allylic carbonium ion), there was ground to hope they would not compete favorably with ring expansion. This expectation was indeed fulfilled, and this paper reports on the reactions the isomeric pairs of sulfonium salts, **1b**, **1c** and **2b**, **2c**, undergo under conditions of methylide formation. [The charges are omitted; **1b**, **1c**, **2b**, and **2c** were triflate or hexafluorophosphate salts (see below).] No cis–trans isomerization of the sulfonium salt precursors appears to accompany such reactions, thus allowing for meaningful stereochemical information to be drawn.



1

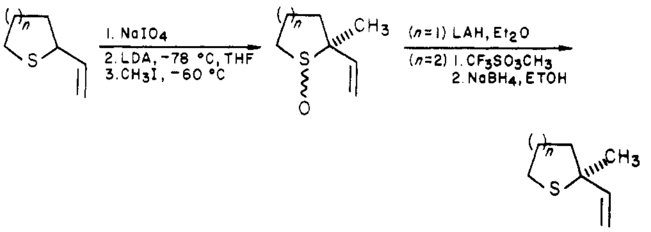


2

a, $R_1 = R_2$ = lone pair; b, $R_1 = CH_3$; $R_2$ = lone pair; c, $R_1$ = lone pair; $R_2 = CH_3$; d, $R_1 = CH_2$; $R_2$ – lone pair; e, $R_1$ = lone pair; $R_2 = CH_2$

## Results

**Preparation of 2-Methyl-2-vinylthiolane and -thiane.** Our synthetic approach used as starting materials the 2-vinyl derivatives of thiolane and thiane, compounds which were known to us[4b] and appeared to offer an easy entry to the desired products via a metalation–alkylation sequence. Three variants were essayed, where the sequence was applied, respectively to the 2-vinyl sulfides themselves, the 1-oxides, and the 1,1-dioxides. The route through the sulfoxide was found to work best and was adopted as outlined below:



The two other variants gave unsatisfactory results and were abandoned. In the first, 2-vinylthiolane was metalated with BuLi in hexane in the presence of tetramethylethylenediamine (TMEDA) and quenched with $CH_3I$ to give three methylation products, including **1a** (10%, GLC). The two addition major products (70%) appeared to be isomeric olefins arising from reaction at the $\gamma$-allylic carbon.

In the second variant, 2-vinylthiolane 1,1-dioxide was subjected to the metalation–alkylation sequence (BuLi–THF/$CH_3I$, -50 °C), giving in excellent yield 2-methyl-2-vinylthiolane 1,1-dioxide. However, all attempts of reducing the latter back to the sulfide were fruitless.

**Preparation and Ring Expansion of Sulfonium Salts 1b, 1c and 2b, 2c.** Methyl triflate treatment of sulfides **1a** and **2a** in $CH_2Cl_2$ gave the corresponding sulfonium triflates as inseparable mixtures of geometrical isomers whose composition was established from the relative intensities of the $SCH_3$ resonances in the $^1H$ NMR spectra. In turn, the configurational assignment was based on the $SCH_3$ $^1H$ shifts, as follows. In the corresponding 1-methyl-2-vinyl salts, it had been previously observed[4b] that the vinyl group shields the $SCH_3$ H's of the cis isomer more than the corresponding H's of the trans isomer (0.25 and 0.15 ppm for the five- and six-membered salts, respectively). Similar differential shieldings occur in the 1,2-dimethyl-2-vinylthiolanium and -thianium salts (though the values are somewhat smaller, 0.19 and 0.10 ppm). On this basis, the isomer of the **1b**, **1c** or **2b**, **2c** pairs having the $SCH_3$ resonance upfield was assigned the **1b** or **2b** configuration, i.e., the vinyl and the $SCH_3$ groups cis to each other. The assignments are consistent with an independent configurational criterion based on the $^{13}C$ shielding of the nonterminal vinyl carbon, CH=. The argument runs as follows. In 1-methyl-2-vinylthiolanium and -thianium salts the CH= resonance occurs at significantly higher field in the cis than in the trans isomers, $\delta_{cis} - \delta_{trans} = -3.7$ and $-1.2$ ppm in the five- and six-membered rings, respectively.[4b] These differential shieldings clearly arise from a $\gamma$-effect by the $SCH_3$ group, which, as it is well documented,[9] is greater in the cis than in the trans isomers. On this basis, in compounds **1b** and **2b**, where the $SCH_3$ and $CH{=}CH_2$ groups are cis to each other, the CH= resonance is expected to occur at higher field than that in the corresponding "trans" isomers **1c** and **2c**. The differential shieldings turn out to be quite sizeable and in the direction expected on the basis of the differential $SCH_3$ proton shifts: $\delta_{1b} - \delta_{1c} = -3.6$ ppm and $\delta_{2b} - \delta_{2c} = -3.4$ ppm.

Conversion of triflates **1b**, **1c** and **2b**, **2c** to crystalline hexafluorophosphates did not improve the isomers' separability, and therefore the mixtures of isomeric salts were

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[5] (a) Vedejs, E.; Mullins, M. J.; Renga, J. M.; Singer, S. P. *Tetrahedron Lett.* **1978**, 519. (b) Schmid, R.; Schmid, H. *Helv. Chim. Acta* **1977**, *60*, 1361.

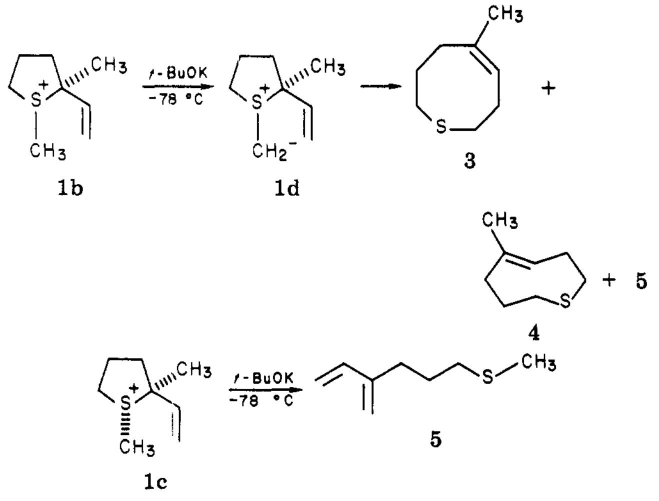
[6] Darwish, D.; Tomilson, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 5938.

[7] Garbesi, A.; Corsi, N.; Fava, A. *Helv. Chim. Acta* **1970**, *53*, 1499 and references therein.

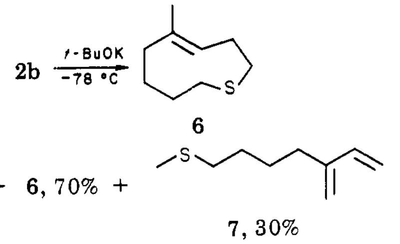
[8] Darwish, D.; Hui, S. H.; Tomilson, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 5631.

[9] (a) Barbarella, G.; Dembech, P.; Garbesi, A.; Fava, A. *Org. Magn. Reson.* **1976**, *8*, 446. (b) Eliel, E. L.; Willer, R. L. *J. Am. Chem. Soc.* **1977**, *99*, 1936. (c) Willer, R. L.; Eliel, E. L. *Org. Magn. Reson.* **1977**, *9*, 285. (d) Barbarella, G.; Dembech, P. *Ibid.* **1979**, *10*, 000.

Scheme I



Scheme II



subjected to ring-expansion conditions by using variable defects of base and examining the product distribution as well as the isomer composition of the recovered unreacted starting material. The results obtained with the five- and six-membered ring sulfonium salts are summarized in Schemes I and II, respectively, and described in detail in the Experimental Section. Of the five-member ring salts **1b** and **1c**, only **1b**, where the 5-methyl and the vinyl groups are on the same side of the ring, undergoes ring expansion. The other isomer, **1c**, gives a ring opened sulfide, **5**, a product of $\beta$-elimination.

The relative configuration of the cyclic products **3** and **4** was readily apparent from the NMR behavior of their single olefinic proton. In the major isomer (**3**) the resonance at $\delta$ 5.41 shows up as a triplet, $J$ = 7.4 Hz, further split into doublets, $J$ = 1.5 Hz. The latter is the long-range allylic coupling to the $C_5$ $CH_3$ H's, and the former must arise from a time-averaged coupling with the adjacent $CH_2$ H's, consistent with the fast conformational change expected for a cis structure. On the other hand, in the minor isomer (**4**) the resonance at $\delta$ 5.17 appears as an octet, $J$ = 9.0, 6.5 and 1.5 Hz, consistent with the nonequivalence of the adjacent $CH_2$ H's expected for the rigid trans isomer. The nature of the elimination product (**5**; $m/e$ 142) was also established on the basis of its NMR behavior. The $^1$H NMR spectrum shows five olefinic protons and only one methyl singlet, $\delta$ 2.10, characteristic of a $SCH_3$ group. The $^{13}$C NMR spectrum shows one quartet and three triplets in the aliphatic region and one singlet, one doublet, and two triplets in the olefinic region (see Experimental Section). Of the $\beta$-elimination products that may conceivably arise from **1c** or **1b**, only one, 4-methylenehex-5-en-1-yl methyl sulfide (**5**), is compatible with these NMR features.

The mixture of isomeric 1,2-dimethyl-2-vinylthianium salts **2b** and **2c** behaved substantially similarly. In this case, however, the [2,3] sigmatropic shift occurred with both isomers, although considerably more rapidly from the "cis" (**2b**) than from the "trans" (**2c**) cation. Moreover, the latter concurrently gave a product of $\beta$-elimination, the ring-opened sulfide **7**.

The trans configuration of **6** was evinced from the $^1$H NMR spectrum showing extensive line broadening at the probe temperature (~35 °C) and already becoming sharp at -30 °C. This is indicative of a (relatively) highly activated exchange process, precisely as expected for a cyclic nine-membered trans olefin.[10-12]

The structure of the elimination product (**7**) was immediately established from its NMR features, substantially identical with those of **5** (see above and Experimental Section).

## Discussion

This study has proven the following. (1) The sulfonium ylides where the carbanionic carbon and the vinyl group are on the same side of the ring, **1d** and **2d** ("cis" ylides), undergo [2,3] sigmatropic shift faster than their "trans" counterparts, **1e** and **2e**. (2) Both isomers of the six-membered methylide, **2d** and **2e**, react completely stereoselectively to give the ring-expanded olefin of $E$ configuration. (3) The five-membered "cis" methylide reacts not only less stereoselectively but also reacts with opposite stereochemistry, the $Z$ olefin being formed preferentially. (4) No product of ring expansion can be observed from the five-membered "trans" methylide **1e**, due to a competing $\beta$-elimination which takes over completely.

Considering the thiolanium methylides first, the greater reactivity of the "cis" ylide could be expected since, as models show, only if the termini of the sigmatropic transition state are on the same side of the five-membered ring can they approach enough to interact effectively. This interaction may take place in either of two geometrical arrangements: a cisoid transition state, $\mathbf{3}^{\ddagger}$, which can be reached with a minimum of deformation from conformation **1d-A** (half-chair ring with maximum torsion at $C_3C_4$, vinyl group quasi-equatorial and rotated inward), and a transoid one, $\mathbf{4}^{\ddagger}$ (from conformation **1d-B**, vinyl group quasi-axial and rotated outward).

From models, $\mathbf{3}^{\ddagger}$, but not $\mathbf{4}^{\ddagger}$, appears to suffer a repulsive interaction, arising from one of the vinyl H's being pushed against and past the quasi-axial H at $C_3$.[14]

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(10) (a) Cope, A. C.; Banholzer, K.; Keller, H.; Pawson, B. A.; Whang, J. J.; Winkler, H. J. S. *J. Am. Chem. Soc.* **1965**, *87*, 3644. (b) Reese, C. B., Shaw, A. *Ibid.* **1970**, *92*, 2566. (c) Reese, C. B.; Shaw, A. *Chem. Commun.* **1970**, 1367. (d) Reese, C. B.; Shaw, A. *J. Chem. Soc., Perkin Trans 1* **1975**, 2422. (e) Loozen, H. J. J.; de Haan, J. W.; Buck, H. M.; *J. Org. Chem.* **1977**, *42*, 418.

(11) The conformational process which inverts the configuration of the chiral plane in *trans*-cyclononene has a barrier of about 20 kcal mol$^{-1}$.[10a] Indeed, substituted *trans*-cyclononenes having an additional chiral center appear to exist as diastereomeric conformers whose equilibration becomes rapid (in the $^1$H NMR time scale) above 90 °C.[10c,d] In our case the coalescence temperature is expected to be considerably lower since the barrier must be significantly decreased due to the presence of the heteroatom.[4a] This expectation is confirmed by a dynamic $^{13}$C NMR study of *trans*-2-methylthiacyclonon-4-ene whose barrier turns out to be about 16 kcal mol$^{-1}$.[13]

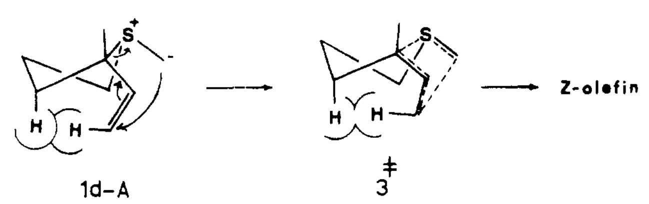
(12) Vedejs has reported that 2-carboethoxy- and 2-vinyl-substituted *trans*-thiacyclonon-4-enes show up as mixtures of conformational isomers on the 100-MHz $^1$H NMR time scale.[3b,c] This observation implies a barrier to conformational inversion somewhat higher than that for our thiacyclononenes, which may perhaps be accounted for in terms of a steric effect by the bulkier 2-substituent.

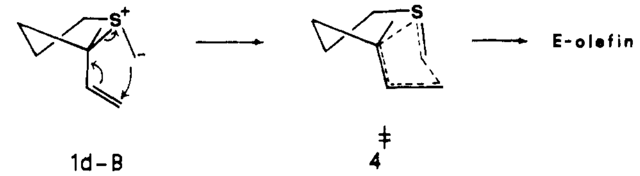
(13) Lunazzi, L., to be submitted for publication.

(14) Although this pictorial representation uses half-chair ring conformations for the ylide,[15] the actual ground-state conformation is immaterial. Models show that a steric interaction of the type depicted in $\mathbf{3}^{\ddagger}$ is present in all reasonable cissoid transition states.

(15) However, this is known to be the preferred conformation of *S*-methylthiolanium cations;[16] there is then a fair chance that it may be preferred by the ylide as well.

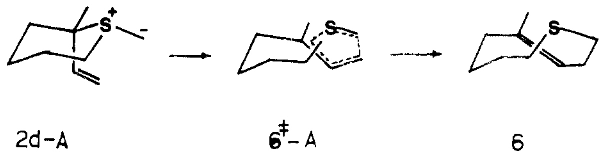
(16) (a) Garbesi, A.; Barbarella, G.; Fava, A. *J. Chem. Soc., Chem. Commun.* **1973**, 155. (b) Barbarella, G.; Garbesi, A.; Boicelli, A.; Fava, A. *J. Am. Chem. Soc.* **1973**, *95*, 8051. Barbarella, G.; Garbesi, A.; Fava, A. *Ibid.* **1975**, *97*, 5883.

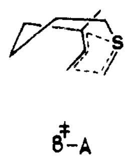




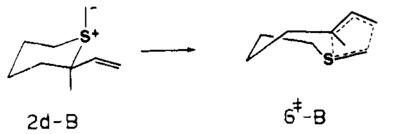
Since in five-membered rings the conformational barriers are very low,[17] probably much lower than those for [2,3] sigmatropic shift, the product isomer distribution will be solely determined by the relative energy of the two transition states. Henceforth, the observation that the *Z* olefin prevails by a factor of 17 (at 195 K) indicates the cisoid transition state has lower energy than the transoid one by about 1.1 kcal mol$^{-1}$. This difference does not necessarily contradict the postulated unfavorable steric interaction in the cisoid transition state but may originate from another steric factor making the transoid transition state still more unfavorable. This can reasonably be the strain arising from the incipient trans double bond in what will eventually become an eight-membered ring.[2] Actually, since the energy difference between the final products, *E* and *Z* olefin, is very large ($\sim$10 kcal mol$^{-1}$)[18] the transition state for [2,3] sigmatropic shift may still be very reactant-like.[1b,21] If this is the case, the *E*/*Z* product ratio could be expected (Hammond postulate) to increase with the transition state becoming even less product like, i.e., with decreasing ylide stability. This expectation appears to be fulfilled insofar as in the ring expansion of the ylides from 1-methyl-[4b] and 1-ethyl-2-vinylthiolanium[4a] cations (ylide stability decreasing in the order), the *E*/*Z* olefin product ratio changes from 1:7 to 1.4:1.

The results obtained with the six-membered ylides, where ring expansion produces the *E* olefin highly preferentially, can also be reasonably accounted for in terms of ground-state effects, in agreement with the idea of a fundamentally early transition state. The sulfonium salt precursor, and most likely the ylide, will populate comparably[22] the two chair conformers **2d-A** and **2d-B**. From **2d-A** a transoid transition state, **6**$^{\ddagger}$**-A**, appears to be most easily accessible as it requires a minimal geometrical adjustment from the ground state. On the other hand, achieving a cisoid transition state from **2d-A** appears to be very difficult. The vinyl group has to be rotated inward and, to bring the carbanionic carbon within bonding distance, the six-membered ring would have to move to a boat conformation. Such transition state, **8**$^{\ddagger}$**-A**, can be definitely ruled out as too unfavorable sterically. Thus from the **2d-A** conformer only the trans ring-expanded product may be expected to obtain.

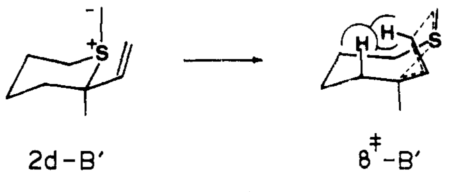




For the other conformer, **2d-B**, the transoid transition state appears to be relatively disfavored. The vinyl group has to be rotated downward where, however, the distance between the termini is too large for interaction; to decrease the distance, the six-membered moiety has to move to a boat shape, as shown in the **6**$^{\ddagger}$**-B**. There is no question that **6**$^{\ddagger}$**-B** has a much higher energy than that of **6**$^{\ddagger}$**-A** so that most, if not all, of the reaction will take place through the latter.



A cisoid transition state would seem to be easily accessible from the **2d-B′** rotamer where the vinyl group is set upward. A closer look to this rotamer, however, shows that the mutual orientation of the $\pi$ system and the carbanion lone-pair orbital is such that for overlap to be obtained, the S–C$_2$ bond has to be twisted somewhat to decrease the C$_6$SC$_2$C$_3$ dihedral angle. While this brings the termini of the sigmatropic reaction in to a suitable geometry for overlap, one of the vinyl H's is required to draw close to the axial H at C$_3$ (ground-state numbering) as shown in **8**$^{\ddagger}$**-B**. This steric interaction may well be responsible for a higher energy of the cisoid (**8**$^{\ddagger}$**-B**) over the transoid (**6**$^{\ddagger}$**-A**) transition state, to the point where the latter becomes the essentially exclusive pathway.[26]



Models show that from **2e-C** only a transoid transition state is accessible (**6**$^{\ddagger}$**-C**), rather different from **6**$^{\ddagger}$**-A**, insofar as, unlike **6**$^{\ddagger}$**-A**, it leads to a boat–chair rather than a twist

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[17] Allinger, N. L.; Hickey, M. J. *J. Am. Chem. Soc.* **1975**, *97*, 5167.

[18] *trans*-Cyclooctene is more strained than *cis*-cyclooctene by 9.3 kcal mol$^{-1}$.[19] The energy difference between *trans*- and *cis*-thiacyclooct-4-ene must be on the same order. Actually, force field computations carried out in this laboratory[20] definitely indicate the strain of *trans*-thiacyclooct-4-ene is about 2.5 kcal mol$^{-1}$ greater than that of *trans*-cyclooctene.

[19] Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.

[20] Guerra, M., unpublished results.

[21] Evans, D. A.; Andrews, G. C. *J. Am. Chem. Soc.* **1972**, *94*, 3672.

[22] That the A and B conformers of **2d** may be comparably populated follows from the following: (i) in the thiane system the S$^+$–CH$_3$ group has a very small conformational energy, 0.2 kcal mol$^{-1}$;[23] (ii) in cyclohexane, the conformational energy difference ($\Delta G_{CH_3} - \Delta G_{CH=CH_2}$) amounts to about 0.3 kcal mol$^{-1}$;[24] (iii) the conformational energy of groups at the 2-position of thiane is considerably smaller than in cyclohexane;[9,17,25] thus the difference, $\Delta G_{CH_3} - \Delta G_{CH=CH_2}$, will be even smaller than 0.3 kcal mol$^{-1}$. In conclusion, the **2d-A** conformer may be somewhat more stable than **2d-B**, but by no more than a few tenths of a kcal mol$^{-1}$.

[23] Eliel, E. L.; Willer, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 3021.

[24] Hirsch, J. A. *Top. Stereochem.* **1967**, *1*, 199.

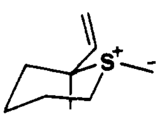
[25] Willer, R. L.; Eliel, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 1925.

[26] Although in the present case no cis ring-expanded olefin could be detected, small percentages of it (4–6%) were observed in the ring expansion of 2-vinylthianium 1-methylide[4b] and 1-ethylide.[13] It is remarkable in this connection that in the ring expansion of cyclic six-membered nitrogen ylides, the geometry of the nine-membered product olefin may be essentially all trans or all cis, depending on subtle variations of the substituents at the N atom.[3b,c]

conformation of the nine-membered ring.

2e-C $6^{\ddagger}$-C 6

Formation of a cisoid transition state from **2e** appears to be prohibitively difficult: the vinyl group would be required to set itself backward (**2e-C′**) where no appreciable interaction can occur with the carbanion lone-pair orbital. On the other hand no purely conformational change may improve the ground-state situation since no conformation exists where trans vicinal substituents may approach each other more than in the chair. Thus the exclusive formation of the trans ring-expanded product from **2e** appears to be completely justified.



2e- C′

One may ask why the trans ylide (**2e**) should react more slowly than the cis one (**2d**). A reasonable explanation may be the following. In the cis ylide the termini of the [2,3] sigmatropic reaction may be made to approach simply by decreasing the endocyclic dihedral angle, $C_6SC_2C_3$, a deformation which requires relatively little energy. In the trans ylide, on the other hand, the same goal would require increasing the endocyclic dihedral angle, an energetically very demanding deformation. Thus, to the extent that the transition state requires that the carbanion and the terminal vinyl carbons get closer together than they are in the ground state, the cis ylide will react more readily. There is a further (and related) motive, which may apply in particular to our system. Because of the gem disubstitution, the ring will tend to flatten somewhat in that region, which implies a decrease of the endocyclic dihedral angle at the S–$C_2$ bond. As a consequence, the termini of the sigmatropic reaction will be drawn closer in the cis and farther in the trans ylide. Thus, less geometrical change, and less energy, will be required to bring the termini of the sigmatropic reaction within interacting distance in the cis than in the trans ylide. In other words, the shorter distance between the termini of the sigmatropic reaction will ensure a stronger incipient bond in the transition state from the cis ylide, the more so, the more "reactant-like" the transition state is.

The relatively low reactivity of **2e** brings back the question of the reactivity of **1e**, the five-membered ring trans ylide. Since in five-membered rings the endocyclic dihedral angles are necessarily smaller, and the divergence angle (from the center of a hypothetical flat ring) necessarily greater, than in six-membered rings, the reacting termini on opposite sides of the ring are farther apart in five- than in six-membered rings. Henceforth it may be concluded that the ring expansion of **1e**, if it could be observed, would be much slower than that of **2e** and hence much slower than that of **1d**.

This conclusion is relevant in connection with the ring expansion of 1-methyl-2-vinylthiolanium and -thianium salts where, under conditions of methylide formation, rapid cis–trans isomerization may occur via reversible abstraction of the allylic proton at $C_2$.[4] It seems safe to conclude that even though the starting sulfonium salt reagent may have the trans configuration, the ring-expanded products arise from the cis isomer essentially exclusively. Our results strongly support the view, also advanced by Vedejs,[3a] that this conclusion applies to stabilized ylides as well. Particularly revealing in this connection is the observation[3b] that while the stabilized six-membered ylides resemble their acyclic analogues in rearrangement rates and yields, the five-membered ones rearrange considerably more slowly with only moderate yields, and side reactions such as Stevens rearrangement often compete.[3b] In view of the trans configuration of Vedejs ylides[2,3] these observations can be easily explained. As we have proven, the six-membered trans ylide may undergo [2,3] sigmatropic rearrangement. The five-membered ones, on the other hand, cannot rearrange unless isomerization to the cis ylide first occurs, which can only take place by reversible abstraction of the allylic proton. Since, however, in the stabilized ylides the allylic proton is not nearly as acidic as the exocyclic protons, isomerization is a *relatively* slow process. Thus other reactions which do not depend on the stereochemistry of the ylide, such as Stevens rearrangement, may successfully compete with [2,3] sigmatropic shift.

A final comment is in order concerning the $\beta$-elimination products **5** and **7**. Although a clear-cut mechanistic choice is not allowed, the observation that they arise principally, if not wholly, from the "trans" sulfonium salt precursors, where the vicinal $CH_3$'s are cis to each other, is strongly suggestive of the $\alpha',\beta$ mechanism.

That elimination occurs more easily from the five- than the six-membered sulfonium salt may be due to the five-membered ring allowing for cis vicinal substituents to be more readily set in the syn coplanar arrangement most favorable for $\alpha',\beta$ elimination. An additional and perhaps more important factor, however, may be the release of strain attending the opening of the five-membered ring.

## Experimental Section

Proton NMR spectra were recorded at 100 MHz on a Varian XL-100 operating in the CW mode. Proton noise decoupled $^{13}C$ spectra were recorded at 25.15 MHz with a Varian XL-100 by the FT technique; single-frequency off-resonance spectra were obtained by irradiation at $\delta - 4$ in the proton spectrum. Unless otherwise stated, $^{1}H$ and $^{13}C$ shifts are given in ppm from $Me_4Si$ in $CDCl_3$ solvent. GLC analyses were carried out with a Hewlett-Packard 5700 instrument equipped with a flame-ionization detector ($^1/_8$ in. × 3 m column, 10% XE 60 on Chromosorb W). Preparative GLC separations were carried out with a Varian-Aerograph 712 instrument ($^3/_8$ in. × 3 m column, 10% XE 60 on Chromosorb W, 60–80 mesh, at 110 °C).

Solvents and reagents were obtained dry as follows. Benzene, methylene chloride, *tert*-butyl alcohol, diisopropylamine, and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) were distilled from calcium hydride, and ethyl ether was distilled from $LiAlH_4$. Tetrahydrofuran, dried over sodium and distilled, was redistilled from $LiAlH_4$ immediately before use. All reactions involving organolithium reagents were carried out under nitrogen, the reagents being introduced by syringe through a rubber stopper.

**2-Vinylthiolane 1-oxide** was prepared in 90% yield by aqueous $NaIO_4$ oxidation[27] of 2-vinylthiolane;[3a] bp 94–96 °C (2 mm). The material gave a single GLC peak; its $^{1}H$ NMR spectrum, particularly the olefinic region, appeared to be too complex,

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(27) Leonard, N. J.; Johnson, C. R. *J. Org. Chem.* **1962**, *27*, 282.

however, for a single terminal vinyl group. Indeed, the $^{13}C$ spectrum showed 12 lines of about equal intensity, consistent with a rougly 1:1 isomeric mixture of cis and trans isomers. No attempt was made to separate the isomers, and the material was used as such in the subsequent alkylation.

**2-Vinylthiane 1-oxide** was obtained in 90% yield from 2-vinylthiane,[3,4b] by the same procedure used for the corresponding thiolane derivative, as a liquid, bp 118 °C (2mm). In GLC the material gave two peaks in a 1:1.5 ratio, and $^{13}C$ NMR confirmed the presence of two isomers approximately in that proportion. The $^{13}C$ shifts (ppm) for the major and (in parentheses) the minor isomer are as follows: CH=, 134.4 (132.8); =CH$_2$, 119.4 (120.6); C$_2$, 59.2 (65.8); C$_6$, 46.3 (50.0); C$_3$, 21.7 (27.3); C$_4$, 24.4 (23.7); C$_5$, 15.2 (21.7). These shifts correspond within few tenths of a part per million to those which may be computed from the known $^{13}C$ substituent effects of the S-O function in the equatorial and, respectively, in the axial conformation,[28] leaving little doubt that the major and minor isomers have the cis (S–O axial) and the trans (diequatorial) configurations, respectively.

The material was used as such in the subsequent alkylation.

**2-Methyl-2-vinylthiolane 1-Oxide.** A THF solution of 2-vinylthiolane 1-oxide (30 mmol in 50 mL; isomeric mixture) was added dropwise at −78 °C to a THF solution of lithium diisopropylamide (LDA), prepared at −78 °C from diisopropylamine in THF (3.03 g, 30 mmol in 50 mL) and 1 equiv of butyllithium in hexane (1.6 M). A deep red color developed which turned yellow after the addition was complete. After 15 min at −78 °C, a THF solution of methyl iodide (1.2 equiv in 10 mL) was added. The temperature was raised to −50 °C, and stirring was continued until the color was discharged (ca. 30 min). After the mixture was quenched with H$_2$O (10 mL), the organic solvent and the amine were removed under reduced pressure, and the aqueous residue was extracted with CH$_2$Cl$_2$ (4 × 50 mL). The combined extracts were dried and evaporated to afford crude 2-methyl-2-vinylthiolane 1-oxide [80%, >90% pure, bp 76–77 °C (0.4 mm)] as a ca. 1:5 mixture of geometrical isomers ($^1H$ and $^{13}C$ NMR) which, after distillation, was used as such in the subsequent reduction. The more remarkable feature of the $^1H$ NMR spectrum is the presence of two Me singlets (1:5 intensity ratio) at $\delta$ 1.43 (minor) and 1.21 (major). On the basis of the well-established deshielding effect of the S-O bond on syn $\beta$-H's,[29] the minor isomer has the Me group cis to O. Thus the methylation of the sulfinyl carbanion(s) from the ca. 1:1 mixture of *cis*- and *trans*-2-vinylthiolane 1-oxide is largely stereoconvergent, and the Me group ends up predominantly trans to oxygen. Nothing can be said about the steric course, except that one isomer reacts with predominant inversion and the other with predominant retention. This question is being further investigated in detail in view of the current interest in the stereochemistry of the alkylation of $\alpha$-lithio sulfoxides.[30]

**2-Methyl-2-vinylthiane 1-oxide** was obtained (80%, > 90% pure) by the same procedure as that described for the lower homologue except that CH$_3$I quenching took place already at −68 °C; bp 86 °C (0.2 mm). The material gave a single GLC peak; however, its $^{13}C$ NMR also revealed the presence of a minor isomer approximately to the extent of 5–8%. The $^{13}C$ (ppm) shifts of the major isomer are as follows: 135.9 (CH=), 118.3 (=CH$_2$), 57.1 (C$_2$), 44.5 (C$_6$), 31.2 (C$_3$), 21.9 (CH$_3$), 20.2 (C$_4$), 19.3 (C$_5$). The $^1H$ NMR (only the major isomer was visible) has the following shifts: $\delta$ 6.17 (q, $J$ = 10.8 and 17.2, 1 H, CH=), 5.52–5.22 (m, 2 H, =CH$_2$), 2.82 (m, 2 H, $\alpha$-CH$_2$), 2.18 (m, 2 H, $\beta$-H′ cis to S-O), 1.65 (m, 4 H, $\beta$-H trans to S-O and $\gamma$-CH$_2$), 1.39 (s, 3 H, CH$_3$). The stereochemistry of the major isomer cannot be assigned on these bases. However, it is likely that in the alkylation of the $\alpha$-lithio sulfoxide the CH$_3$ group enters trans to S-O.[30b]

**2-Methyl-2-vinylthiolane (1a).** An ether solution of the isomeric mixture of 2-methyl-2-vinylthiolane 1-oxides (1.44 g, 10 mmol, in 100 mL) was added dropwise over 30 min to a suspension of LiAlH$_4$ in ether (1.18 g, 31 mmol, in 100 mL) maintained at ca. 20 °C and the reaction allowed to proceed for 20 min. The reaction mixture was ice cooled, quenched with 20% aqueous NH$_4$Cl, and filtered. The aqueous layer was extracted with ether and the extracts combined with the ether layer to afford, after drying and evaporation, 1.15 g (90%) of crude 2-methyl-2-vinylthiolane (ca. 80% pure; three additional minor peaks of comparable retention time were visible in GLC). Attempted purification by distillation failed to remove the impurities. The pure title compound was obtained by column chromatography (SiO$_2$, pentane–benzene, 9:1): bp 74–75 °C (25 mm); $^1H$ NMR $\delta$ 6.03 (q, $J$ = 9.4 and 17.8, 1 H, CH=), 5.3–4.9 (m, 2 H, =CH$_2$), 3.0 (t, 2 H, $\alpha$-CH$_2$), 2.3–1.7 (m, 4 H, $\beta$-CH$_2$'s), 1.52 (s, 3 H, CH$_3$); $^{13}C$ NMR 145.6 (CH=), 111.0 (=CH$_2$), 57.3 (C$_2$), 44.5 (C$_3$), 33.5 (C$_5$), 29.8 (C$_4$), 27.9 ppm (CH$_3$). Anal. Calcd for $C_7H_{12}S$: C, 65.57; H, 9.43. Found: C, 65.63; H, 9.31.

**2-Methyl-2-vinylthiane (2a).** Attempted LiAlH$_4$ reduction of 2-methyl-2-vinylthiane 1-oxide according to the procedure outlined above for the thiolane analogue was unsuccessful, insofar as only unreacted sulfoxide was recovered. Higher temperature (reflux) and/or longer contact times (12 h) led to complex mixtures of unidentified products containing only a small amount (10–20%) of the desired sulfide. Similarly unsatisfactory results were obtained by using sodium bis(2-methoxyethoxy)aluminohydride (Red-Al) as reducing agent in benzene at 35–50 °C for up to 3 h. Reduction of the sulfoxide to **2a** was eventually achieved by the Johnson and Phillips method via the alkoxysulfonium salt.[31] Methyl triflate (1.84 g, 11 mmol) was added to a solution of 2-methyl-2-vinylthiane 1-oxide (1.58 g, 10 mmol) in 75 mL of CH$_2$Cl$_2$ at 0 °C. After 30 min the temperature was raised to 20 °C and the reaction allowed to proceed for 90 min. After removal of solvent, the viscous residue was taken up with 50 mL of EtOH. To the solution, warmed at 40 °C, was added NaBH$_4$ (0.19 g, 10 mmol) portionwise. After 15 min the solvent was evaporated and the residue extracted with H$_2$O/pentane. The aqueous layer was extracted with pentane, and the combined organic layers, after drying and evaporation, gave 1.06 g of the title compound (75%, >95% pure): bp 89–90 °C (30 mm); $^1H$ NMR $\delta$ 5.89 (q, $J$ = 10.4 and 17.3, 1 H, CH=), 5.45–5.05 (m, 2 H, =CH$_2$), 2.59 (m, 2 H, $\alpha$-CH$_2$), 1.72 (m, 6 H, $\beta$- and $\gamma$-CH$_2$'s), 1.31 (s, 3 H, CH$_3$); $^{13}C$ NMR 144.2 (CH=), 113.3 (=CH$_2$), 44.5 (C$_2$), 39.6 (C$_3$), 28.4 (CH$_3$), 26.9–26.6 (C$_5$ and C$_6$, interchangeable), 22.4 ppm (C$_4$). Anal. Calcd for $C_8H_{14}S$: C, 67.54; H, 9.92. Found: C, 67.42; H, 10.01.

**1,2-Dimethyl-2-vinylthiolanium Hexafluorophosphates 1b and 1c.** To a solution of crude **1a** (1.28 g, 10 mmol) in 80 mL of CH$_2$Cl$_2$ at 0 °C was added a solution of methyl trifluoromethanesulfonate (1.65 g, 10 mmol, in 5 mL of CH$_2$Cl$_2$) dropwise over 10 min. After 2 h at 0 °C the solvent was removed, and the residue was dissolved in 10 mL of H$_2$O. Aqueous ammonium hexafluorophosphate was added (10 mmol in 5 mL), and the crude sulfonium hexafluorophosphate was recovered by CH$_2$Cl$_2$ extraction and purified by repeated crystallization from hot absolute ethanol. However, at each crystallization step part of the compound was lost in the form of a solid, probably polymeric material, insoluble in boiling EtOH. The salt (1.7 g, 59%) is a highly hygroscopic crystalline material which, from $^1H$ and $^{13}C$ NMR, appears to be a ca. 7:3 mixture of geometrical isomers. Their ratio appears not to change on repeated crystallization.

The minor component, however, could be later obtained in isomerically pure form by recovering the sulfonium salt left unreacted after ring expansion with a defect of base (see below). It has the following characteristics: $^1H$ NMR (acetone-$d_6$ solvent) $\delta$ 6.20 (q, $J$ = 10.6 and 17.4, 1 H, CH=), 5.75–5.44 (m, 2 H, =CH$_2$), 3.93 and 3.52 (2 m, each extending over 0.5 ppm, 1 H each, $\alpha$-H's), 2.98 (s, 3 H, SCH$_3$), 2.5 (m, 4 H, $\beta$-H's), 1.82 (s, 3 H, CCH$_3$). The $^{13}C$ NMR (acetone-$d_6$ solvent, in parentheses the values for the major isomer) data are as follows: CH=, 138.3 (134.7); =CH$_2$, 120.0 (122.5); C$_2$, 72.7 (72.8); C$_3$, 45.1 (45.4); C$_5$, 40.0 (38.6); C$_4$, 27.6 (27.4); CCH$_3$, 21.8 (24.5); SCH$_3$, 21.2 ppm (23.9).

From the $^1H$ NMR of the isomeric mixture, the major isomer appears to have the SCH$_3$ and the CCH$_3$ singlets at $\delta$ 2.80 and 1.77, respectively. These data identify the minor and the major isomer as **1c** and **1b**, respectively. (For arguments in support of

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[28] (a) Buchanan, G. W.; Durst, T. *Tetrahedron Lett.* **1975**, 1683; (b) Barbarella, G.; Dembech, P.; Garbesi, A.; Fava, A. *Org. Magn. Reson.* **1976**, *8*, 108.

[29] Lett, R.; Marquet, A. *Tetrahedron* **1974**, *30*, 3379 and references therein.

[30] (a) Biellmann, J. F.; Vicens, J. J. *Tetrahedron Lett.* **1978**, 467. (b) Bory, S.; Marquet, A. *Ibid.* **1978**, 471. (c) Cerè, V.; Pollicino, S.; Sandri, E.; Fava, A. *Ibid.* **1978**, 5239.

[31] Johnson, C. R.; Phillips, W. G. *J. Org. Chem.* **1967**, *32*, 3233.

this assignment, see the Results section).

**1,2-Dimethyl-2-vinylthianium hexafluorophosphates 2b and 2c** were prepared as described for **1b** and **1c** from 2-methyl-2-vinylthiane (1.42 g, 10 mmol) as a white crystalline hygroscopic material (2.56 g, 85%; mp 140–143 °C) which appears to be a ca. 1:1.5 mixture of diastereomers. Contrary to its lower homologue this salt is quite stable to boiling ethanol; however, the isomer distribution does not change on further crystallization. A sample of the minor isomer, mp 145–147 °C, could be obtained in pure form, however, by recovering the sulfonium salt left unreacted after ring expansion with a defect of base (see below). The minor component appears to have the following characteristics: $^1$H NMR (acetone-$d_6$) $\delta$ 6.26 (q, $J$ = 11.0 and 17.0 Hz, 1 H, CH=), 5.92–5.63 (m, 2 H, =$CH_2$), 3.6 (m, extended over 0.5 ppm, 2 H, $\alpha$-$CH_2$), 3.03 (s, 3 H, $SCH_3$), 1.78 (s, 3 H, $CCH_3$), the $\beta$- and $\gamma$-$CH_2$ overlap with the solvent resonance in a region comprised between 2.2 and 1.9; $^{13}$C NMR 137.6 (CH=), 121.7 (=$CH_2$), 56.7 ($C_2$), 35.7 and 34.8 ($C_6$ and $C_3$, interchangeable), 20.8, 19.8, 19.1, and 17.8 ppm, ($CCH_3$, $C_5$, $C_4$, and $SCH_3$, interchangeable). From the $^{13}$C spectrum of the isomeric mixture of salts the shieldings of the major isomer could be obtained: 134.0 (CH=), 123.4 (=$CH_2$), 56.0 ($C_2$), 35.0 and 33.2 ($C_6$ and $C_3$, interchangeable), 22.8, 20.0, 19.3, and 18.3 ppm ($CCH_3$, $C_5$, $C_4$, and $SCH_3$, interchangeable). From the $^{13}$C shieldings of the CH= vinyl carbon in the two isomers, the major isomer can be assigned the **2b** structure. (For the argument in support of this assignment, see the Results section.)

From the $^1$H NMR of the 1:1.5 isomeric mixture two important features may be evinced of the major isomer, i.e., the $SCH_3$ and $CCH_3$ singlets, occurring at $\delta$ 2.93 and 1.84.

**Ring Expansion of 1c and 1b in the Presence of a Defect of Base. *cis*- and *trans*-5-Methylthiacyclooct-4-ene.** A solution of 2.88 g (10 mmol) of a 7:3 mixture of **1b** and **1c** (see above) in 80 mL of THF/*t*-BuOH (10/1) was treated at −78 °C with *t*-BuOK (0.952 g, 8.5 mmol, 15% defect). After 2 h at −78 °C the mixture was quenched with 5 mL of $H_2O$ and extracted with pentane to remove the sulfide products. The aqueous residue, after evaporation of the organic solvents under reduced pressure, was twice extracted with $CH_2Cl_2$ to recover the unreacted sulfonium salt (0.8 g). Its $^1$H NMR spectrum showed the major isomer was completely absent, the material essentially consisting of the minor isomer **1c**.

After removal of solvent the pentane extracts gave 0.9 g of a mixture of three isomeric sulfides (*m/e* 142) in the ratio 1:10:0.6, which were separated by preparative GLC. The major product appears to be *cis*-5-methylthiacyclooct-4-ene (**3**): $^1$H NMR $\delta$ 5.41 (td, $J$ = 1.5 and 7.4 Hz, 1 H, olefinic proton), 2.5 (m, extending over 0.4 ppm, 8 H), 1.85 (m, extending over 0.3 ppm, 2 H), 1.63 (dd, $J$ = 1.5 and 0.5 Hz, 3 H, $CH_3$); $^{13}$C NMR 137.3 (CH=), 124.5 (=$CH_2$), 35.1 ($C_2$), 31.0, 30.8, 29.6, and 28.3 ($C_3$, $C_6$, $C_7$, and $C_8$, interchangeable), 22.5 ppm ($CH_3$). Anal. Calcd for $C_8H_{14}S$: C, 67.54; H, 9.92. Found: C, 67.62; H, 9.83.

The minor product appears to be *trans*-5-methylthiacyclooct-4-ene (**4**): $^1$H NMR $\delta$ 5.17 (ddd, $J$ = 1.5, 6.5, and 9.0 Hz, 1 H, olefinic proton), 2.6 (m, extended over 1.2 ppm, 10 H, $\alpha$-, $\beta$-, and $\gamma$-$CH_2$'s), 1.82 (d, $J$ = 1.5 Hz, broadened by a second small splitting of 0.2 Hz, 3 H, $CH_3$); $^{13}$C NMR 141.4 ($C_5$), 125.8 (=$CH_2$), 44.5 ($C_2$), 41.3 ($C_6$), 35.7 and 35.0 ($C_7$ and $C_8$, interchangeable), 32.0 ($C_3$), 18.9 ppm ($CH_3$).

The third product could be unequivocally identified from its NMR as a ring opened sulfide, 4-methylenehex-5-en-1-yl methyl sulfide (**5**): $^1$H NMR $\delta$ 6.40 (q, $J$ = 10.4 and 18.0 Hz, 1 H, =$C_5H$), 5.18 (m, extending over 0.3 ppm) superimposed to a 5.03 singlet (4 H overall, =$C_6H_2$ and $C_4$=$CH_2$, respectively), 2.53 (t, $J$ = 7.0 Hz, 2 H, S–$CH_2$), 2.34 (m, 2 H, $C_3H_2$), 2.10 (s, 3 H, $SCH_3$), 1.78 (m, 2 H, $C_2H_2$); $^{13}$C NMR 145.6 ($C_4$), 138.8 ($C_5$), 116.1 ($C_4$=$CH_2$), 113.4 ($C_6$), 34.0 ($C_1$), 30.4 ($C_3$), 27.6 ($C_2$), 15.5 ppm ($CH_3$).

Before the above-described ring expansion experiment was performed, two other experiments had been carried out with a 30% defect of base at −40 °C and at −78 °C, respectively. In the −40 °C experiment, the **5**:**3**:**4** product ratio (GLC) was ca. 1:3:0.2, and the sulfonium salt recovered was ($^1$H NMR) a ca. 1:1 mixture of **1b** and **1c**. In the −78 °C experiment, the product ratio was ca. 1:14:0.7, and the unreacted sulfonium salt had a **1b**:**1c** ratio of ca. 1:4. These results suggest the elimination reaction is relatively favored at high temperature and occurs mainly, if not exclusively, with the **1c** isomer. Indeed, when the isomerically pure sample of **1c** (recovered from the ring-expansion experiment first described) was subjected to ring-expansion conditions at −78 °C, the sulfide fraction was found to contain the ring-opened sulfide **5** with no appreciable amounts of ring-expanded products. This latter experiment only proves that **1c** does not undergo ring expansion competitive with $\beta$-elimination. It cannot exclude, however, that the ring-opened sulfide may not form, though in a small percentage, from **1b** as well.

**Ring Expansion of 2b and 2c in the Presence of a Defect of Base. *trans*-5-Methylthiacyclonon-4-ene (6).** The 1.5:1 mixture of **2b** and **2c** (1.5 g, 5 mmol) was treated at −78 °C with *t*-BuOK (0.336 g, 3 mmol, 40% defect) as described for the thiolanium analogues to yield 0.350 g (89% based on *t*-BuOK) of a crude sulfide which gave a single peak in GLC (*m/e* 156). The recovered unreacted sulfonium salt (0.56 g, 75% based on **2c**) appeared to be isomerically pure **2c** (see above) which was crystallized from EtOH; mp 145–147 °C. The $^1$H NMR spectrum of the sulfide fraction shows, at the probe temperature (~35 °C), only two sharp resonances, $\delta$ 5.42 (td, $J$ = 7.6 and 1.3 Hz, 1 H, olefinic proton) and 1.70 (d, $J$ = 1.3 Hz, 3 H, $CH_3$). The rest of the spectrum shows only a broad unresolved absorption extending from $\delta$ 3.2 to 1.1 (12 H) with flat maxima at $\delta$ 2.6, 2.3, 2.1, and 1.6. When the temperature is lowered, the absorption in this region gets sharper, and the spectrum does not undergo any further change below −30 °C. [This behavior is precisely that expected for a nine-membered cyclic olefin of trans configuration (see Results section and ref 12)]. The resonances in this region could not be assigned, however, due to strong coupling. The low-field triplet (of doublets) did not change its appearance on lowering the temperature down to −80 °C. Since ring inversion is undoubtedly frozen at this temperature, the olefinic proton triplet was expected to become an AXY quartet. Since it did not, it may be that, accidentally, $J_{AX} \simeq J_{AY}$. The $^{13}$C spectrum shows nine lines: 137.0 ($C_5$), 123.0 ($C_4$), 17.9 ($CH_3$); the remaining resonances, unassigned, are at 40.4, 37.8, 36.4, 29.5, 28.1, 26.7 ppm. No low-intensity lines are apparent which may be assigned to the *Z* olefin. Thus the *E* olefin is formed with an isomeric purity of better than 95%. Anal. Calcd for $C_9H_{16}S$: C, 69.18; H, 10.32. Found: C, 69.31; H, 10.20.

**Ring Expansion of 2c.** The **2c** sample recovered from the above experiment carried out with a defect of base, subjected once more to ring-expansion conditions with 1.2 equiv of *t*-BuOK at −78 °C for 2 h, failed to give ring-expanded products in an appreciable amount and was recovered unchanged. The same sample (0.35 g, 1.16 mmol) was then subjected to ring-expansion conditions for 2 h at −40 °C and worked up. The recovered sulfonium salt (0.02 g, 6%) was isomerically pure **2c**. The sulfide fraction (0.16 g, 93% based on **2c** consumed) gave two GLC peaks in a ca. 7:3 intensity ratio (both *m/e* 156). The major product was the ring-expanded trans olefin **6**. The $^{13}$C NMR of the reaction mixture shows the minor product also has nine lines, four of which are in the olefinic region. From the $\delta$ values and the splitting pattern it was readily identified as the ring-opened sulfide 5-methylenehept-6-en-1-yl methyl sulfide (**7**): $^{13}$C NMR 146.1 ($C_5$); 138.9 ($C_6$); 115.8 ($C_5$=$CH_2$); 113.2 ($C_7$); 34.2 ($C_1$); 31.0 ($C_4$); 29.0 ($C_2$); 27.2 ($C_3$); 15.5 ppm ($CH_3$). The $^1$H NMR of the **6** and **7** mixture allows the identification of some of the features of the ring-opened sulfide which are consistent with the proposed structure: $\delta$ 6.44 (q, $J$ = 17.8 and 10.2, $C_6H$), 2.09 (s, $SCH_3$).

**2-Vinylthiolane 1,1-dioxide** was obtained as an oily material by oxidation of 2-vinylthiolane with excess aqueous $NaIO_4$: $^1$H NMR $\delta$ 6.2–5.2 (m, 3 H, vinyl protons), 3.70 (m, 1 H, $C_2$ H), 3.1 (m, 2 H, $C_5H_2$), 2.15 (m, 4 H, $\beta$-$CH_2$'s).

**2-Methyl-2-vinylthiolane 1,1-Dioxide.** To a THF solution of 2-vinylthiolane sulfone (1.46 g, 10 mmol, in 20 mL) at −50 °C was added 1 equiv of BuLi in hexane (1.6 M) dropwise. After 15 min 1 equiv of $CH_3I$ was slowly added while the temperature rose to −40 °C. Stirring was continued until the color was discharged. After being quenched with water and extracted with $CH_2Cl_2$, the solution was dried and evaporated to yield an oil (1.2 g, 75%) whose $^1$H NMR is consistent with the title compound: $^1$H NMR (60 MHz) $\delta$ 6.10 (q, $J$ = 17.1 and 10.3, 1 H, CH=), 5.4 (m, 2 H, =$CH_2$), 3.1 (m, 2 H, $\alpha$-$CH_2$), 2.2 (m, 4 H, $\beta$-$CH_2$'s), 1.44 (s, 3 H, $CH_3$). Anal. Calcd for $C_7H_{12}SO_2$: C, 52.47; H, 7.55. Found: C, 52.30; H, 7.25.

**Attempted Reduction of 2-Methyl-2-vinylthiolane 1,1-Dioxide.** To a suspension of $LiAlH_4$ in $Et_2O$ (1.52 g, 40 mmol, in 100 mL) under nitrogen was added an ether solution of the sulfone (0.8 g, 5 mmol, in 50 mL) and the mixture warmed at reflux. GLC monitoring showed the slow disappearance of the sulfone peak was accompanied by the appearance of the **1a** peak, together with several other unidentified peaks of comparable magnitude. After 5 h, while unreacted sulfone was still present, the fraction of **1a** in the product was ~15%. No better results were obtained by changing the hydride/sulfone molar ratio. Similarly unsatisfactory results were obtained when the sulfone was allowed to react with 10 equiv of Red-Al in benzene at 80 °C for 2 h.

**Methylation of 2-Vinylthiolane.** To 10 mmol of the butyllithium–TMEDA complex[32] (1.6 M in hexane) at -10 °C was added 2-vinylthiolane (1.14 g, 10 mmol) dropwise. A yellow precipitate formed almost immediately while the temperature rose to -5 °C. (Attempted metalation at lower temperatures, -50 to -20 °C, for various lengths of time, followed by $CH_3I$ quenching, led only to the recovery of unreacted 2-vinylthiolane, indicating metalation had not occurred at these low temperatures.) After 15 min at -5 °C, the temperature was brought down to -50 °C, and 10 mL of THF was added which dissolved the precipitate. Methyl iodide (1.2 equiv) was then added slowly, and stirring was continued until discoloration was complete. Conventional $H_2O/CH_2Cl_2$ workup gave, after drying and evaporation of the solvent, 1.00 g of an oil which on TLC appears to consist of at least three products. The $^1H$ NMR of the crude product shows clearly the $\delta$ 1.52 $CH_3$ singlet of **1a**, from the intensity of which the fraction of **1a** could be estimated at ca. 10%. Besides some unreacted starting material (~20%), two additional major species were present, accounting for the remaining 70% of the product. The presence in the $^1H$ NMR of two high-field triplets at $\delta$ 0.96 and 1.00 ($J$ = 7.0 Hz) and their corresponding quartets at $\delta$ 2.05 and 2.02, respectively, suggests these species may be products of $\gamma$-alkylation, i.e., isomeric (*E*)- and (*Z*)-2-(1-propylidene)thiolane.

**Registry No. 1a**, 71411-24-0; **1b**, 71411-26-2; **1c**, 71411-28-4; **2a**, 71411-29-5; **2b**, 71411-31-9; **2c**, 71411-33-1; **3**, 71411-34-2; **4**, 71411-35-3; **5**, 71411-36-4; **6**, 71411-37-5; **7**, 71411-38-6; *cis*-2-vinylthiolane 1-oxide, 71434-87-2; *trans*-2-vinylthiolane 1-oxide, 71434-88-3; *cis*-2-vinylthiane 1-oxide, 71434-89-4; *trans*-2-vinylthiane 1-oxide, 71434-90-7; *cis*-2-methyl-2-vinylthiolane 1-oxide, 71434-91-8; *trans*-2-methyl-2-vinylthiolane 1-oxide, 71434-92-9; methyl iodide, 74-88-4; *cis*-2-methyl-2-vinylthiane 1-oxide, 71434-93-0; *trans*-2-methyl-2-vinylthiane 1-oxide, 71434-94-1; ammonium hexafluorophosphate, 16941-11-0; 2-vinylthiolane 1,1-dioxide, 71411-39-7; 2-vinylthiolane, 57565-42-1; 2-methyl-2-vinylthiolane 1,1-dioxide, 71411-40-0; (*E*)-2-(1-propylidene)thiolane, 71411-41-1; (*Z*)-2-(1-propylidene)thiolane, 71411-42-2.

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(32) Eberhardt, G. G.; Butte, W. A. *J. Org. Chem.* **1964**, *29*, 2928.

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# Chemistry of Sulfenic Sulfonic Thioanhydrides. Solvent-Dependent Sulfur Extrusion[1]

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Certain sulfenic sulfonic thioanhydrides (**1**) have been found to undergo spontaneous desulfurization to thiosulfonates (**3**) in polar solvents. Further, a novel feature of the chemistry of **3** was discovered in that these thiosulfonates have a tendency to undergo exchange in solution. Mechanisms involving solvent-stabilized sulfenium ions are proposed for both phenomena.

Although sulfenic sulfonic thioanhydrides (**1**)[2] have been known for over 50 years,[3] the chemistry of this class of compound has received little study. Displacement reactions with a variety of nucleophiles have been briefly investigated, and nucleophilic attack at sulfenyl sulfur to displace the thiosulfonate anion appears to be the major reaction pathway (eq 1).[3a-c] More recently, interactions

$$\underset{\mathbf{1}}{RSO_2SSR'} \xrightarrow{Nu^-} R'SNu + RSO_2S^- \tag{1}$$

with trivalent phosphorus compunds have been examined.[3e,f] On the basis that thiosulfinates RS(O)SR′ (**2**),[4a] thiosulfonates $RSO_2SR'$ (**3**),[4b,c] and disulfonic thioanhydrides $RSO_2SSO_2R'$ (**4**)[4c] are deoxygenated by triphenylphosphine to the corresponding disulfide or trisulfide, it might be expected that **1** would be a viable precursor of trisulfides. However, earlier work demonstrated that desulfurization by triphenylphosphine precedes deoxygenation in **1**.[3e,f] Reaction with tris(diethylamino)phosphine is interesting in that desulfurization is followed by formation of a phosphonium salt, demonstrated for **1a** (R, R′ = $4\text{-}CH_3C_6H_4$).[3f] The tendency for **1** to be desulfurized is further revealed in the conversion of **1b** to the corresponding thiosulfonate, after more than ten recrystallizations from ethanol (eq 2). Sulfur-35 labeling experiments have demonstrated that in this "spontaneous" extrusion of sulfur, and in the desulfuriza-

$$\underset{\mathbf{1b}}{4\text{-}CH_3C_6H_4SO_2S^{35}S(4\text{-}NO_2C_6H_4)} \xrightarrow{CH_3CH_2OH} 4\text{-}CH_3C_6H_4SO_2{}^{35}S(4\text{-}NO_2C_6H_4) + S^0 \tag{2}$$

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(1) Organic Sulfur Chemistry. 33. Part 32: D. N. Harpp, T. Aida, and T. H. Chan, *Tetrahedron Lett.*, 2853 (1979).

(2) IUPAC name; also known as sulfenyl thiosulfonates and sulfonyl disulfides and may be considered as partially oxidized trisulfides.

(3) (a) L. G. S. Brooker, R. Child, and S. Smiles, *J. Chem. Soc.*, 1384 (1927). (b) J. D. Loudon and A. Livingston, *ibid.*, 896 (1935). (c) O. Foss, *Acta Chem. Scand.*, **1**, 307 (1947). (d) The strong fungitoxic and phytotoxic properties of trichloromethanesulfenic arenesulfonic thioanhydrides have been demonstrated: J. H. Uhlenbroek and M. J. Koopmans, *Recl. Trav. Chim. Pays-Bas*, **76**, 657 (1957). (e) Y. Abe, T. Nakabayashi, and J. Tsurugi, *Bull. Chem. Soc. Jpn.*, **44**, 2744 (1971). (f) D. N. Harpp, J. G. Gleason, and D. K. Ash, *J. Org. Chem.*, **36**, 322 (1971). (g) The formation (9% yield) of 2-methylpropane-2-sulfenic benzenesulfonic thioanhydride ($PhSO_2SSBu\text{-}t$) in the sulfide-catalyzed decomposition of *tert*-butyl benzenethiosulfinate has been recently reported: T.-L. Ju, J. L. Kice, and C. G. Venier, *J. Org. Chem.*, **44**, 610 (1979).

(4) (a) J. F. Carson and F. F. Wong, *J. Org. Chem.*, **26**, 1467 (1961). (b) L. Horner and H. Nickel, *Justus Liebigs Ann. Chem.*, **597**, 20 (1955). (c) S. Hayashi, M. Furukawa, J. Yamamoto, and K. Hamamura, *Chem. Pharm. Bull.*, **15**, 1310 (1967).

0022-3263/79/1944-4135$01.00/0